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ADVANCED MATERIALS FOR ULTRAHIGH TEMPERATURE STRUCTURAL APPLICATIONS ABOVE 2000° C

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INTRODUCTION

The primary incentive for developing ultrahigh temperature materials for liquid bi-propellant rocket engines lies in the minimization and/or elimination of fuel-film and regenerative cooling of combustion chambers. Cooling is currently required because the most commonly used material for rocket combustion chambers is niobium alloy coated with disilicide with upper limit of operation up to 1450° C which is only approximately 50 % of the propellant combustion temperature (Figure 1) [1]. Therefore, by developing an ultrahigh temperature material with temperature capabilities in the range of 2200 - 3000° C, the fuel-film and regenerative cooling can be significantly reduced and/or eliminated resulting in cleaner burning of rocket engine. Thus fuel utilization can be vastly improved, more payload can be sent to space, higher specific impulse (I_{sp}) can be achieved and finally the cost of the rocket engine could be reduced.

Bi-propellant liquid rocket engines are used for placing and keeping communication, weather and surveillance satellites in a wide range of space orbits as well as for planetary exploration. Therefore, these rocket engines must operate for many hours of burn time with many start times while consuming thousands of kilograms of propellant. Hence, the materials for these rocket engines must have high melting point, resistant to oxidation, good thermal shock properties, low coefficient of thermal expansion (CTE), low vapor pressure especially at elevated temperature, as well as good creep and fatigue properties. The possible candidate materials which can be used at

2200 - 3000 °C are shown in Table I. The evaporation rate for the different materials 2206 °C in a vacuum environment is listed in Table II. There is no single material which possesses all the above listed desired high temperature physical, mechanical and structural properties in a rocket engine environment. Thus, the general approach has been to select a combination of materials where one the load bearing material, the second is for structural purpose and the third is for thermal barrier as well as for oxidation protection of materials.

The existing reusable thermal protection materials for hypersonic space vehicles have maximum operating temperature near 1650 °C due to the fact that all of these materials incorporate silica or derivatives of silica as the essential oxidation protection compounds. For example, the rigid tile and flexible blanket materials used on the Space Shuttle are largely silica in content, and the carbon-carbon leading edge and nose cap materials have a silicon carbide coating for oxidation protection [2]. While silica is an excellent oxidation barrier at temperatures below 1600 °C, above this temperatures the material begins to soften dramatically and develop a substantial vapor pressure. Therefore, both silica and silicon carbide based thermal protection systems are limited in their temperature capability to near 1600 °C in an oxidizing atmosphere. New material systems that can operate as oxidation-resistant thermal barrier structures with temperature capabilities from 2200 - 2700 °C need to be developed.

There are relatively few refractory oxides that are stable in an oxidizing atmosphere above 2000 °C as shown in Figure 2 [3-5]. Of these that are stable, most have characteristics that either limit or preclude their use above 2000 °C. For example, although oxide-based (simple or complex) ceramics are often chemically inert, they are more brittle and more susceptible to thermal shock than the non-oxide based ceramics. Thoria is radioactive and beryllia is markedly toxic. Other oxides with high melting points, such as MgO, CaO and Cr₂O₃, exhibit high evaporation rates or produce high vapor pressures when reacting with oxygen, and are therefore unsuitable for structural applications. A few refractory oxides, such as zirconates and hafnates, also suffer high volatility loss. La₂O₃, MgO and CaO are also hygroscopic and are subject to structural degradation if exposed to atmospheric moisture. Hafnia (melting point 2900 °C) and zirconia (melting point 2770 °C) have sufficiently high melting points and relatively low vapor pressures compared to other oxides. However, they undergo solid phase transformations: from monoclinic to tetragonal structure at 1150 °C and 1650 °C and from tetragonal to cubic at 2370 °C and about 2700 °C for zirconia and hafnia respectively, with a corresponding large volume change. The large volume change would result in the destruction of any large scale component made from these materials, and so in practice the materials must be stabilized with an appropriate additive such as calcium oxide, magnesium

oxide, or yttrium oxide. It has been shown that while the stabilizing additives can substantially improve the mechanical properties, they also lower the melting and softening temperatures. Furthermore, even when stabilized, hafnia and zirconia appear to be still quite susceptible to thermal shock.

This paper outlines and discusses the capabilities of potential material systems either individually or in combination with other materials and their applications in ultra-high temperature and high vacuum environments. Issues and challenges for developing such structural materials for ultrahigh temperature applications will also be detailed and discussed.

REFRACTORY METALS AND ALLOYS

Of all the refractory metals, rhenium (Re) possess a unique combination of properties that makes it a promising candidate material for applications demanding high temperature strength, wear and erosion resistance [6]. Its melting temperature of 3180°C exceeds all other metals except tungsten. However, unlike tungsten, rhenium has a ductile to brittle transition temperature well below room temperature. Also, rhenium has the highest tensile and creep rupture strength at elevated temperature when compared to other refractory metals as illustrated in Figure 3 [5]. With approximately 35 % ductility at room temperature and tensile strength dropping from 1172 Mpa at room temperature to 50 Mpa at 2700°C , rhenium is virtually inert to thermal shock. Rhenium also possesses a wear resistance second only to osmium among the metallic elements and it has the highest strain hardening coefficient of any metal. The two primary methods for fabricating rhenium are powder metallurgy (P/M) and chemical vapor deposition (CVD). Studies show little difference between the mechanical properties of CVD rhenium and those of P/M rhenium. However, due to the difficulties encountered in the P/M fabrication and shaping of rhenium components, CVD is often the preferred method for fabricating thin-walled, small diameter or complex shape components. Recently Low Pressure Plasma Spraying (LPPS) technique and to a lesser extent Spin Forming have become viable and cost effective in comparison to CVD for fabricating near net shape and intricate geometry space components from Rhenium.

The primary drawbacks of rhenium include high cost, high density (22 g/cm^3), poor machinability and low oxidation resistance at elevated temperature. The oxidation resistance of Re and other refractory metals is illustrated in Figure 4 [3]. Re, which forms a low melting point oxide at 266°C , has a high oxidation rate, which is six orders of magnitude higher than that of rhodium, the lowest of the refractory metals. The oxidation resistance can be improved by applying a thin layer of iridium protective coating. Iridium is chosen because it has a high melting temperature (2440°C) and

has a very low oxygen permeability up to 2100 °C. For example, an iridium-coated rhenium rocket thruster has been fabricated by CVD and tested at 2200 °C for 100,000 thermal cycles using a monomethylhydrazine/nitrogen tetroxide propellant system. Re/Ir thrust chambers greatly increase the thermal margin over state-of-the-art silicide-coated niobium thruster by increasing the allowable operating temperature to 2204 °C (4000 F) [7]. The lifetime of a Re/Ir thruster appears to be controlled by the diffusion of rhenium into the hot iridium combustion surface, resulting in severe oxidation.

Other rhenium-based alloys and cermets, such as Re-W, Re-Mo and Re-ceramics may also possess suitable characteristics for ultrahigh temperature applications. For example, several cermets based upon Re and ceramic compounds have been tested for applications in inert or vacuum environment at temperature greater than 2200 °C (Table III)[8]. However, little work has been conducted on developing rhenium-based alloys and cermets. It is expected that significant improvements in the strength, creep resistance and environmental resistance of rhenium could be achieved by utilizing solution, precipitation and dispersion-strengthening alloy additions. Clearly, more fundamental work needs to be conducted. Effort is also required to improve the existing processing technology or to develop alternative manufacturing routes for reducing the fabrication cost.

REFRACTORY CARBIDES

Refractory carbides of Hf, Zr and Ta etc. are potential candidates for ultra high temperature structural applications since they have melting temperatures considerably higher than their associated oxides, do not undergo any solid phase transformation, and have relatively good thermal shock resistance. They are also known to have high strength at high temperature as indicated in Figure 5 [4,5]. However, refractory metal carbides exhibit brittle to ductile transition in the temperature range from 1725 to 1980 °C, depending on stoichiometry [4].

Very limited studies have been conducted to investigate the oxidation behavior of refractory carbides at temperatures above 2000 °C[9-12]. The oxidation resistance of various refractory carbides is illustrated in Figure 7. The oxidation processes of refractory carbides have been shown to be the combined processes of oxygen inward or metal ion outward diffusion and gaseous (or liquid at relatively lower temperatures) by-product outward diffusion through the oxide scale. Therefore, the oxidation resistance of carbides and borides is mainly influenced by the formation and escape of gaseous by-products (such as CO, CO₂) during the oxidation processes which are significantly different from those of their metal counterparts. Several

researchers [10-12] have indicated that hafnium and zirconium carbides (probably tantalum carbide) can readily absorb large quantities of oxygen into the lattice. This indicates that the oxidation process for hafnium, zirconium and tantalum carbides includes nontrivial absorption and diffusion of oxygen into the lattice as preliminary step. Typically, the oxide scale formed at high temperature consists of at least two distinctive layers: (1) a much less porous inner oxide layer and (2) a porous outer oxide layer. However, Bargeron et al. indicated that, in the oxidized HfC film, an oxycarbide ($\text{HfO}_{2-x}\text{C}_y$) interlayer was found between the outer porous HfO_2 layer and a residual carbide layer with dissolved oxygen in the lattice [11]. The oxide interlayer was found to be a better diffusion barrier for oxygen than either the hafnium oxide or carbide layers. Various diffusion models have also been proposed to describe the oxidation behavior of refractory carbide and borides. Holcomb et al. proposed a counter-current gaseous diffusion model to describe the oxidation behavior of HfC [13]. Bargeron et al. proposed an oxidation model for HfC based on moving-boundary diffusion theory [9].

Attempts have also been made to improve the oxidation resistance of refractory carbides with appropriate additives. For example, the high temperature oxidation of HfC-TaC and HfC-PrC₂ composites in the temperature range of 1400-2200 °C was studied by Courtright et al. [10] and Patterson et al [1]. The expectation of better oxidation protection from the oxide scale that forms from HfC mixed with TaC is based on the high temperature oxidation behavior of Hf/Ta alloys [14]. It was found that the oxide layers that formed on HfC-TaC obeyed parabolic growth kinetics. However, there was a break in the kinetics around 1800 °C. The oxidation kinetics of HfC-TaC above 1800 °C were in fair agreement with those reported for the Hf-Ta alloys. Nevertheless, below 1800 °C, the notable difference between the oxide layer that formed on the carbide and the metallic alloy system was observed. The Hf-Ta alloy formed a dense, tenacious oxide layer that contained a small amount of glassy phase to aid in the sealing of cracks and defects. Metal-rich Ta stringers in the ordered Widmanstradtten (lamella) pattern appeared throughout the tetragonal HfO_2 surface layer. Whereas the carbide developed an oxide that was quite porous and prone to cracking. The oxide layer that formed on the carbide was a mixture of HfO_2 and $\text{Ta}_2\text{Hf}_6\text{O}_{19}$ (>1900 °C). Around 1800 °C, the outermost oxide layer was found to be Ta_2O_5 . This indicated that the diffusion coefficient of Ta ion through the oxide is greater than that of Hf ion at this condition.

Courtright et al. [10] also investigated the effect of adding rare-earth elements, such as praseodymium to hafnia to stabilize the pyrochlore structure $\text{Hf}_2\text{Pr}_2\text{O}_7$. The pyrochlores have ionic mobilities that are an order of magnitude lower than that of the high temperature fluorite phase and have melting temperature above 2300 °C. Thus, if an oxide of the pyrochlore

can be grown from a mixed carbide, it might provide better oxidation protection than a pure HfO_2 layer. However, due to the absence of pyrochlore structure in the oxidation products of HfC , this material oxidized at greatly enhanced rates because of the increased void fraction and the inability of growing oxide to form a protective layer. Clearly, greater effort is needed to investigate the effect of additives elements or compounds on the high temperature sinterability and oxidation behavior of refractory carbides.

REFRACTORY BORIDES

Refractory metal borides of Ti, Zr, Hf and Ta have attractive properties that render them of potential value for ultrahigh temperature structural applications [15]. These properties including high melting temperature and high hardness as a result of strong covalent bonding characteristics, low volatility, and high thermal and electrical conductivity. Borides exhibit good thermal shock resistance when compared to other ceramics due to their high thermal conductivity and high elastic modulus. The bend strengths of TiB_2 , ZrB_2 and HfB_2 as a function of temperature (in inert environment) are shown in Figure 6. As expected, the strengths of the refractory borides are widely scattered.

The oxidation resistance of some borides is surprisingly good despite the formation of a fluid B_2O_3 protective layer as shown in Figure 7 [2]. Tripp and Graham reported that liquid B_2O_3 glass formed below 1100°C where the oxidation kinetics are parabolic [16]. Above 1000°C , B_2O_3 vaporizes rapidly, thus reducing its effectiveness as a diffusion barrier. Above 1400°C the rate of vaporization becomes comparable to the rate of formation of B_2O_3 . Bargeron et al. showed that HfB_2 formed a relatively compact hafnium oxide film when oxidized at 1520°C [9]. However, near the boiling point of boric oxide (1860°C), large voids and stove-pipes formed in the oxide layer, indicating a prominent gaseous pressure in the film. The large voids and other paths through the oxide provide an easy access to the interface where the oxidation take place, creating additional gaseous products that must be allowed to escape through the interface..

Attempts have also been made to improve the oxidation resistance of refractory borides with appropriate additives. For example, it has been reported that the addition of SiC can improve the oxidation resistance of both HfB_2 and ZrB_2 [4,16]. The effect of SiC addition on the oxidation of ZrB_2 up to 1500°C was studied by Tripp et al. [16]. The experimental results showed that in the temperature range of $1300 - 1500^\circ\text{C}$, SiC additions to ZrB_2 improve its oxidation resistance. The SiO_2 -rich glassy layer was found to be the outermost oxide layer, whereas ZrO_2 -rich oxide layer was the inner oxide layer. The formation of this glass continue to provide oxidation resistance at

high temperature due to good wettability and surface coverage. The oxidation behavior of ZrB₂/SiC composite in the temperature range of 1800-2400 °C has been studied by Bull et al.[17]. The experimental results confirmed that silicon oxide was formed as the outermost layer, while zirconium oxide was formed as the inner oxide layer. Silicon carbide coexisted with zirconium oxide in the internal oxidation region. The oxidation resistance of HfB₂-SiC at elevated temperatures is also excellent as shown in Figure 7.

Recently, a continuous SiC fiber reinforced ZrB₂-SiC matrix composite has been fabricated and tested as multiple-use heat shields for trans-atmospheric vehicles [18]. The incorporation of high strength, high stiffness SiC fiber is expected to improve the mechanical reliability without compromising the ablation resistance of the ZrB₂-SiC. The bend strength of a 35 v% SCS-9 fiber reinforced ZrB₂-SiC composite is also plotted in Figure 6 for comparison. Obviously, the strength of the fiber-reinforced composite is significant higher than the monolithic matrix material. The preliminary arc-jet ablation test results demonstrated that the SiC fiber reinforced material out-performs the refractory carbon/carbon and silica base ablative material. However, due to the difficulties in aligning the SiC fiber and in densifying the composite, the full potential of the fiber-reinforced composite has not been realized. More research work is needed to optimize the processing and densification conditions to further improve the performance of the fiber-reinforced composite.

CARBON-CARBON COMPOSITES

Carbon-carbon (C-C) composites possess a unique combination of desirable properties, including high strength to weight ratio, resistance to extreme thermal shock, very low coefficient of thermal expansion, as well as excellent strength retention and creep resistance over a wide temperature range [19]. As shown in Figure 8, C-C composite exhibits the highest specific strength when compared to several metallic alloys and ceramic matrix composites from room temperature to over 2000 °C. Based upon their mechanical performance, C-C composites have been identified as attractive structural materials for aeropropulsion applications where temperatures may exceed 2000 °C. However, the use of C-C composites as high temperature structural materials is very limited because of its extremely poor performance in an oxidizing environment, especially above 350 °C. As a result, the development of reliable oxidation protection is crucial to utilizing the full potential of C-C composites.

It is generally accepted that oxidation can be inhibited by minimizing the impurities in the carbon source material, increasing the extent of

graphitization, employing internal oxidation inhibitors and employing an oxidation protection coating. Coatings based on metal carbides and metal oxides, coupled with internal inhibitors are currently being used to provide reasonable oxidation resistance up to 1600 °C. A comprehensive discussion of ceramic coating for C-C composites can be found in references 2 and 19.

However, the presently available coating systems have not proven satisfactory at temperature exceeding 1700 °C. Compounds of Hf, Zr and Th have been developed as coating materials and/or has been impregnated into the surface of C/C composites for oxidation protection. For example, coatings of HfC, HfC/SiC, HfC/HfB₂, HfB₂, HfTaB₂ and Ir/Re have been evaluated to protect carbon-based materials for very short time where SiC and Si₃N₄ cannot be used. Newman reported that the HfC-infiltrated C-C composites could survive exposure to 2760 °C (5000 °F) in oxidizing flow for periods exceeding 10 minutes [20]. More recently, HfC/TaC has been infiltrated into a carbon fiber preform for rocket thruster applications [1].

Long-term oxidation protection of carbon-based materials at very high temperature remains a very challenging problem. Strife et al. [2] proposed that a potential high temperature oxidation protection scheme would involve a coating system consisting of a refractory oxide outer layer for erosion protection, a silica glass inner layer for oxygen diffusion barrier and crack sealant, another refractory oxide inner layer for isolation from the carbon surface, and a refractory carbide inner layer for a carbon diffusion barrier. While such a multilayer coating possess the necessary chemical stability, the deposition of such a coating in a consistent manner is certainly a problem. Likewise, the high thermal expansion coefficient of the coating relative to C-C composites will create severe mechanical compatibility problems in thermal shock. It is clear that basic research is needed to identify new materials and material combinations for long-term oxidation protection at very high temperature.

SUMMARY

Advanced ultrahigh temperature materials are critical to the development of next generation rocket engines and hypersonic spacecrafts. Progress has been made towards identifying, developing and testing of materials individually or in combinations for the applications in the temperature range of 2200- 3000 °C. The Iridium/Rhenium layered materials have been tested in the rocket engine environment at and above 2200 °C and the test results have been outstanding. However, there is an upper temperature limit of 2350 °C for Ir/Re above which material removal rate becomes a critical factor. Also, SiC/SiC composite has proven to be very successful up to 1600 °C. Therefore, a concerted research effort and considerable investment of resources is needed for the development of

ultrahigh temperature materials for low thrust liquid rocket propulsion and hypersonic spacecraft applications. The critical research areas to be investigated are:

- (a) role of additives on the oxidation resistance of refractory metals and their carbides and borides.
- (b) develop cost-effective processing and manufacturing technology to fabricate a dense, near-net-shape ceramic component.
- (c) develop a standardized technique(s) throughout the space industry for the performance evaluations of these materials.
- (d) in-situ characterization of the morphology of the materials during testing at elevated temperatures.
- (e) Free flow and sharing of the technical information between government and industrial research laboratories and universities and to establish a materials databank.

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Table 1

Refractory Metals, Tungsten, Rhenium, Molibdenum and Tantalum

Carbon-Carbon composite, Oxidation inhibited C-C composite

Ceramic -Matrix Composites, C-SiC, SiC-SiC, Si_3N_4 -SiC, C-HfC, C-HfC+SiC and C-HfC+TaC

Cermets and Intermetallics compounds,
 Y_2O_3 , HfO_2 , $\text{ZrO}_2 + \text{M}$
HfC, NbC, TaC, ZrC + M
 ZrRe_2 , HfIr_3 and ZrIr_3

Table 2
Evaporation of materials at 2206 $^{\circ}$ C and 10^{-8} mm torr

Materials	Loss-Mils/hour
HfC	Nil
Tungsten	0.00025
Rhenium	0.0040
Carbon	N/A
Iridium	1.0
Molybdenum	2.0
ZrO ₂	3.0
Al ₂ O ₃	40.0
Rhodium	50.0
Platinum	60.0
BeO	100.0
MgO	8.0
SiO ₂	>10,000
BN	>10,000

Table3

Compounds	Melting Point.
ZrRe3	3020
HfIr3	2737
ZrIr3	2535
ZrPt3	2470
HfPt3	2400
ZrRe2	2170

Table 4

Cermets Test Temperature 0C Compatibility Test Resultss

Re + ThO ₂	2350	Very Good
Re + HfO ₂ + Y ₂ O ₃	2350	Good
Re + ZrO ₂ + Y ₂ O ₃	2350	Good
Re + HfN ₂	2500	Very Good
Re + TaB ₂	2350	Poor
Re + NbB ₂	2250	Poor
Re + HfC	2500	Very Good
Re + NbC	2500	Very Good
Re + TaC	2500	Very Good
Re + ZrC	2500	Very Good

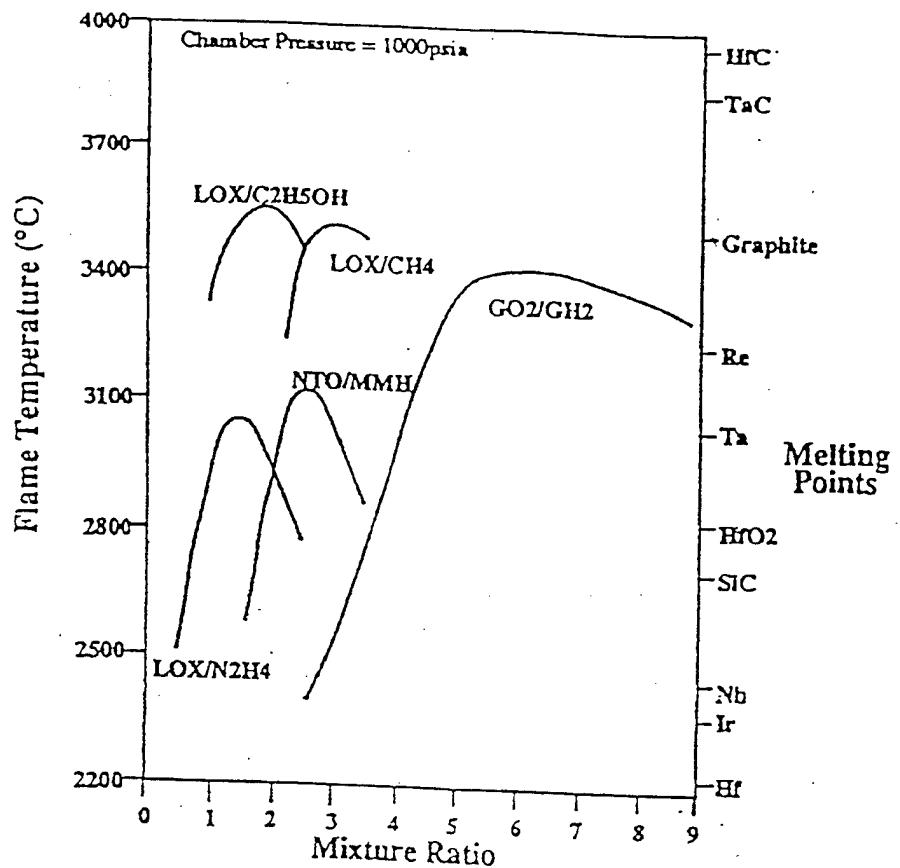


Figure 1 Combustion flame temperatures for several bipropellant fuels for rocket engine

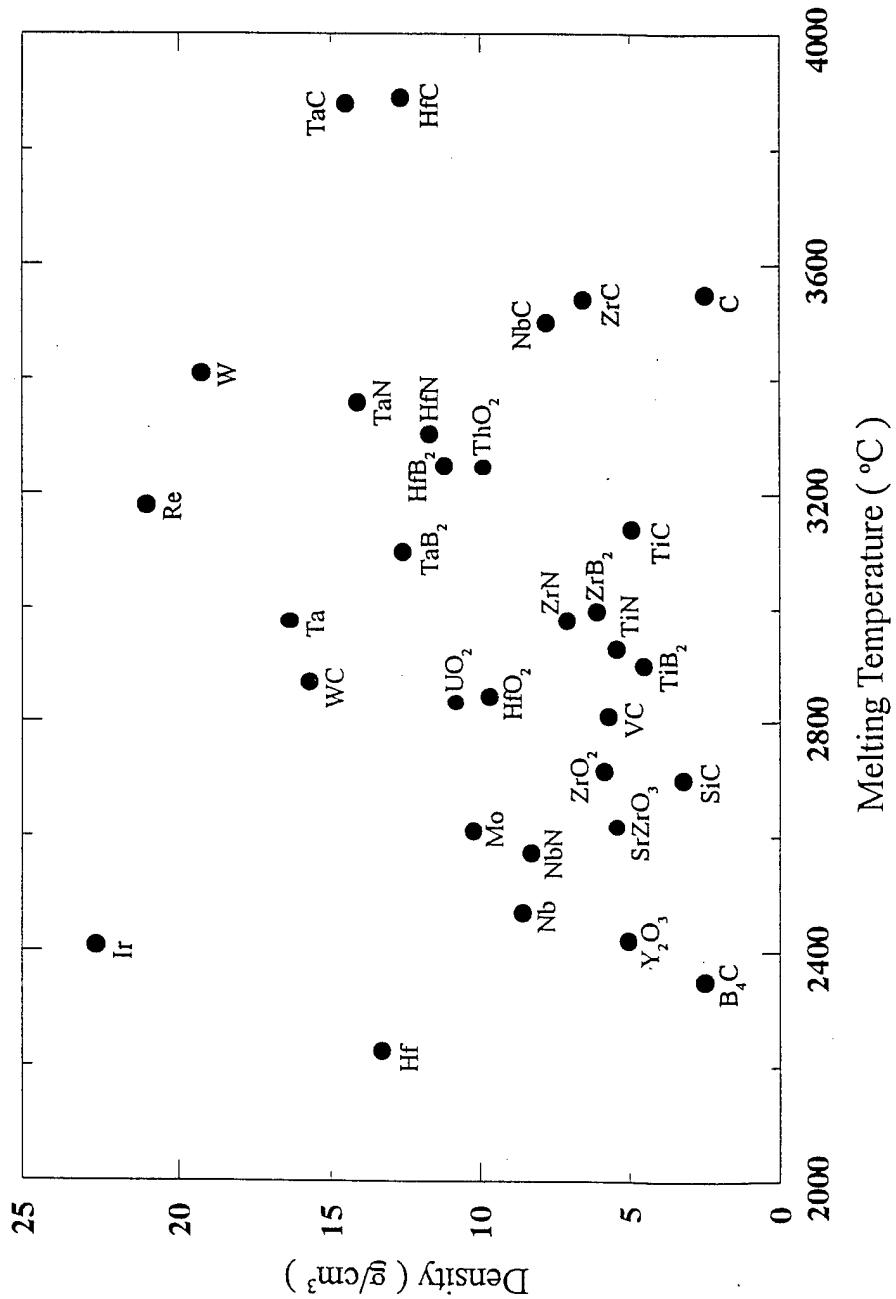


Figure 2 Density vs melting temperature for various high temperature materials

Figure 2

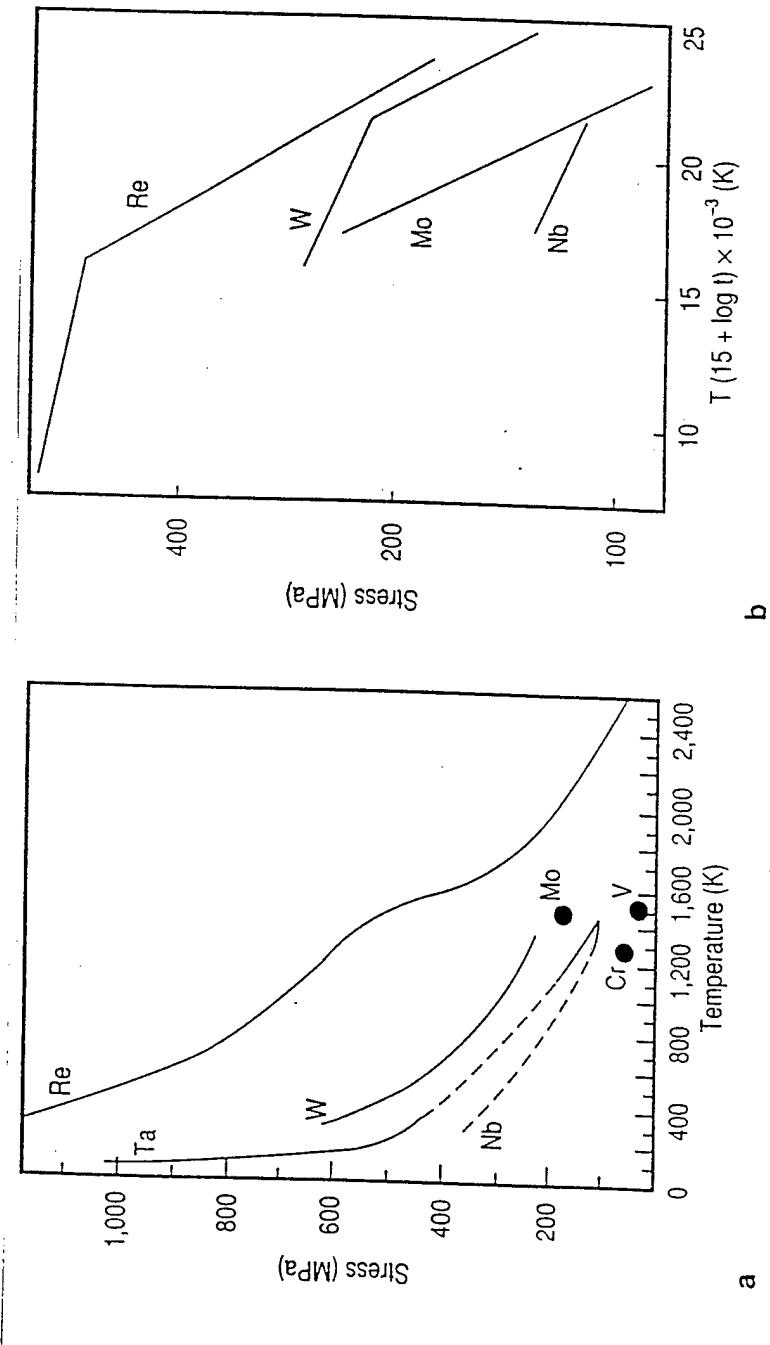


Figure 3 (a) The tensile strength and (b) creep rupture properties of Re and other refractory metals.

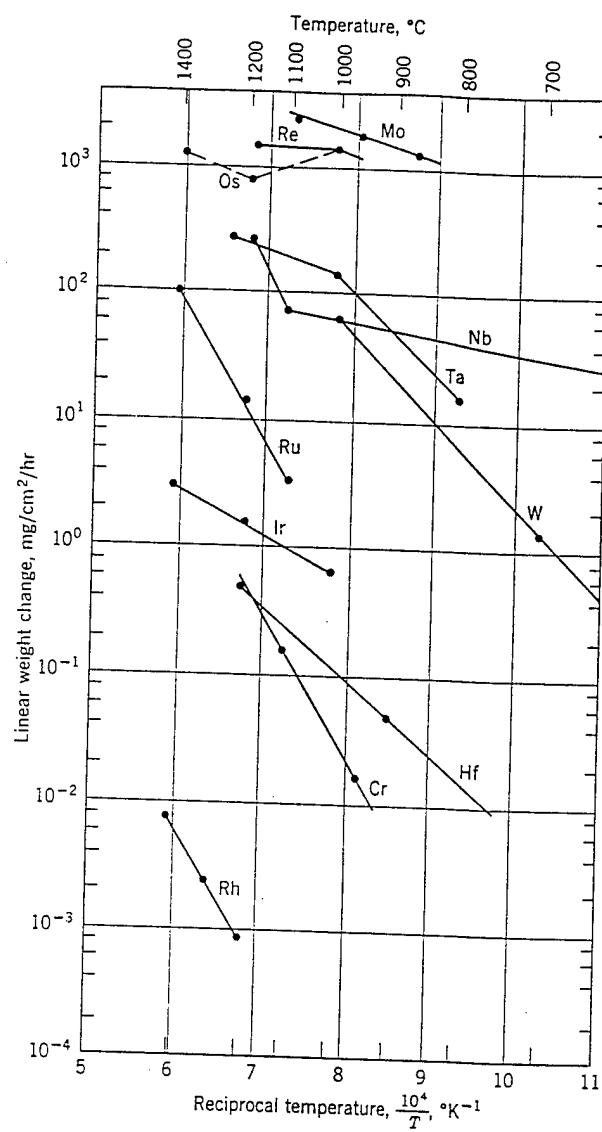


Figure 4 Oxidation of refractory metals. (Data for Mo, Re, Os, Ru, Ir and Rh are weight-loss rates.)

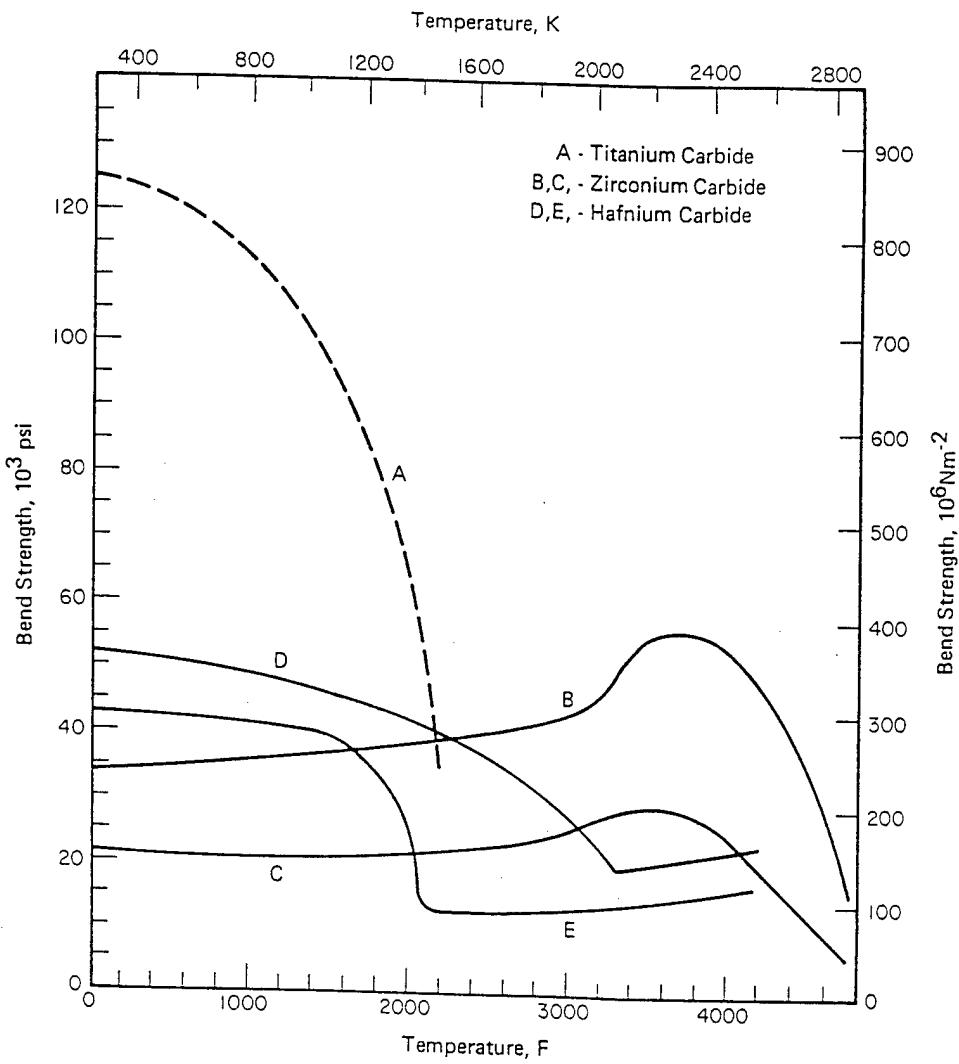


Figure 5 Flexural strengths of refractory carbides

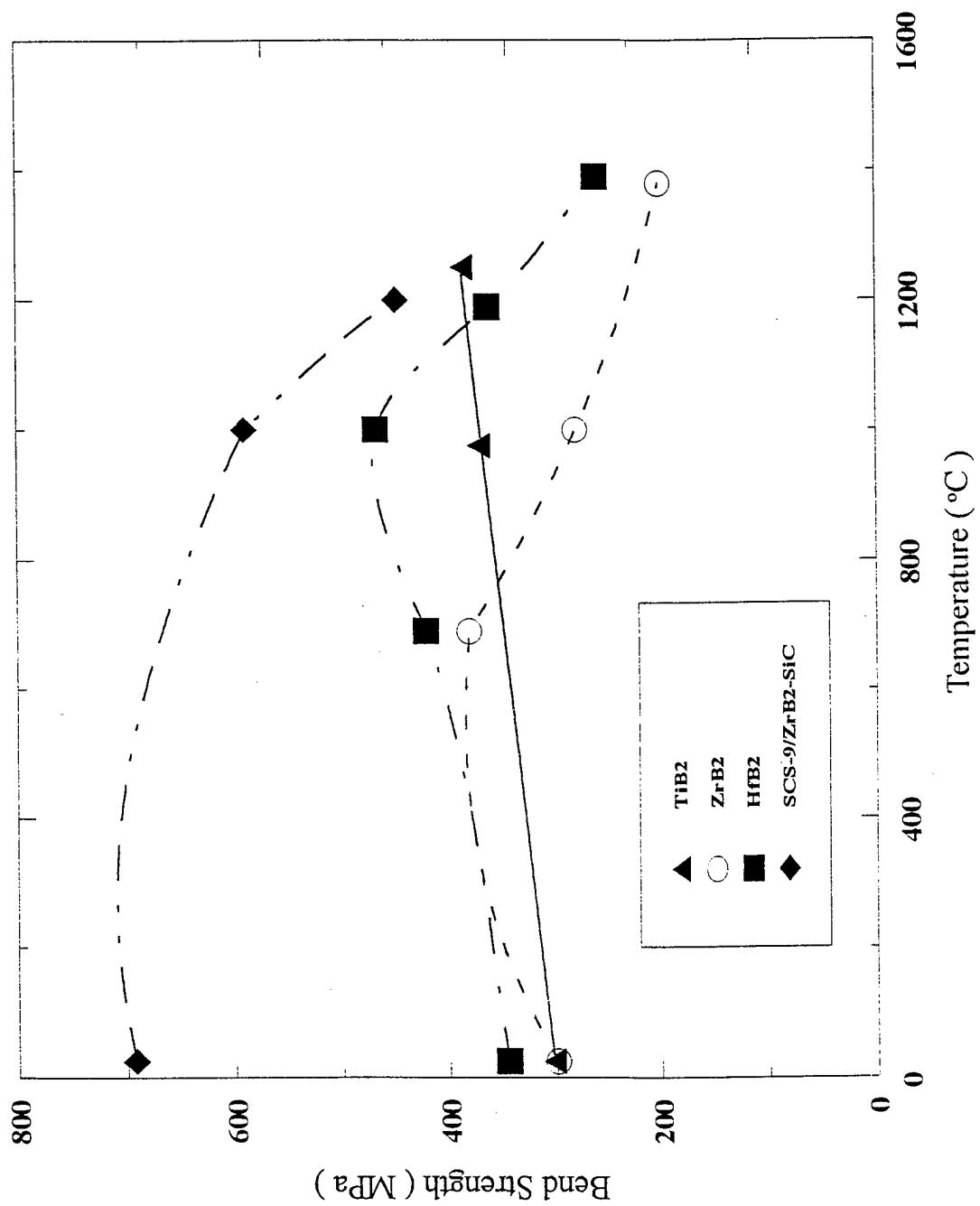


Figure 6 Flexural strengths of refractory borides and composites

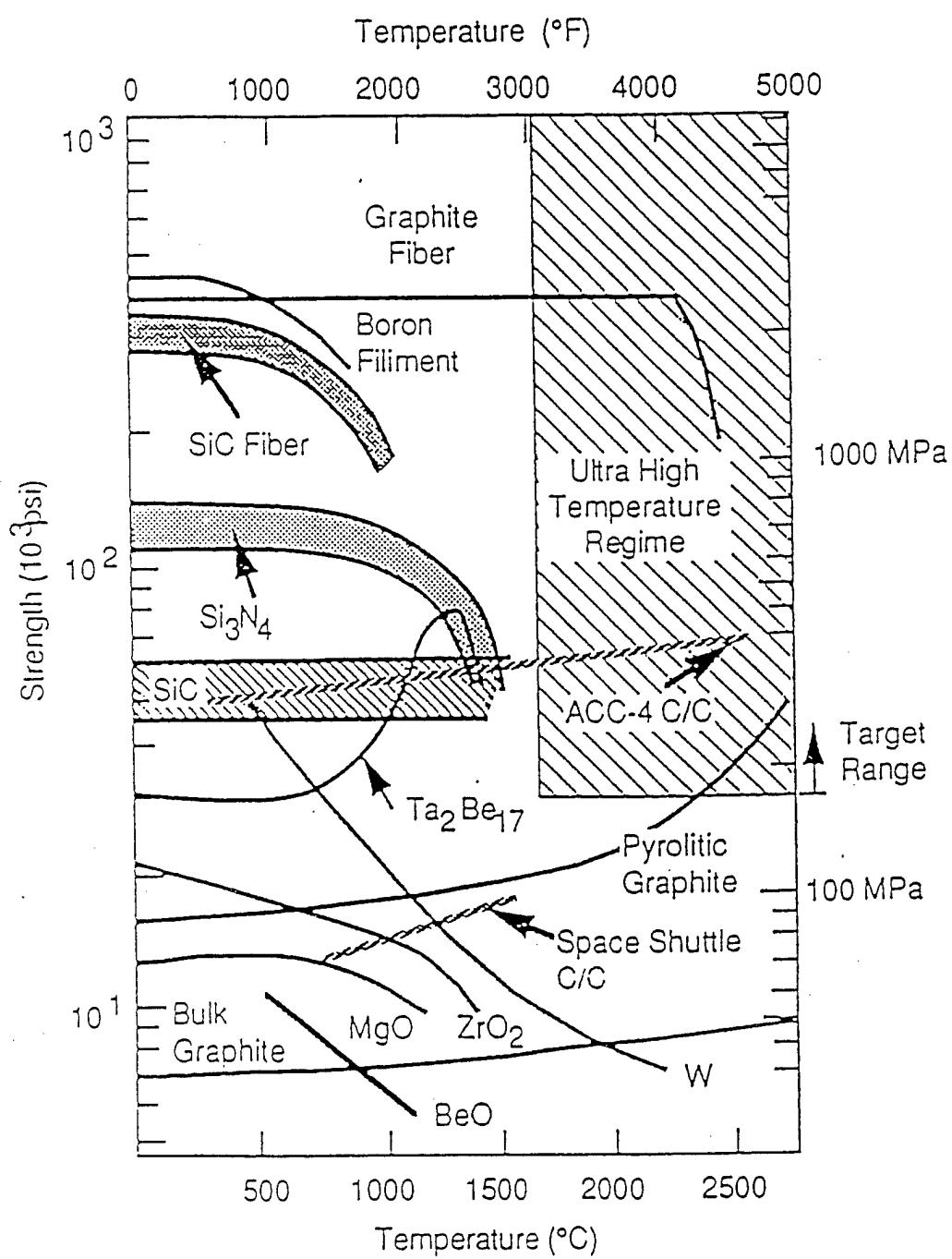


Figure 8 Tensile strengths of carbon-carbon composites and other high temperature materials